

Energy Goals and Challenges for Future Space Exploration

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Outline

- Power Needs for Exploration
- Technology Programs to Achieve Safe and High Energy Power Goals
- Summary and Conclusions



Power Goals and Challenges

 Future exploration needs include very high energy density (~500 Wh/kg) batteries

 Batteries need to be safe under credible off-nominal conditions (no venting, fire, thermal runaway)

Need modular power systems to go across different

applications

Space vehicles

Astronaut Suit

Surface mobility systems

Habitats



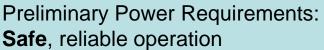






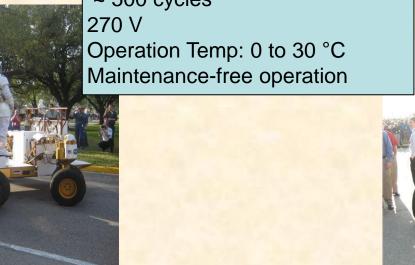
Surface Systems (Mobility) Pressurized Rover





>150 Wh/kg at battery level

~ 500 cycles





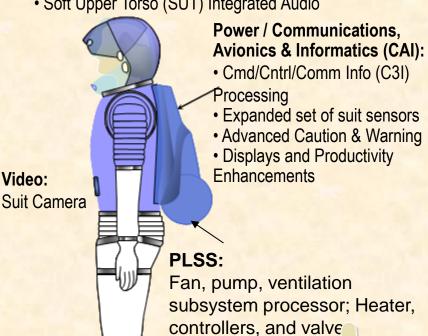
(Advanced) Extravehicular Activity (EVA) Suit

Enhanced Helmet Hardware:

Lighting

Video:

- Heads-Up-Display
- Soft Upper Torso (SUT) Integrated Audio



Power to support 8-hour EVA provided by battery in Portable Life Support System

- Preliminary battery design goals:
 - Human-safe operation
 - 144 W (average) and 233 W (peak) power

Assumes 1% connector loss and 30% margin for growth in power requirements

- No more than 5 kg mass and 3 liter volume
- 100 cycles (use every other day for 6 months)
- 8-hour discharge to at most 85% depth-of-discharge
- Temperature controlled to 0 to +30 °C
- Secondary batteries are considered <u>critical</u> for EVA Suit 2.

Enhanced Liquid Cooling Garment:

Bio-Med Sensors

PLSS: Primary Life Support System

Current Suit Batteries:

EMU: 20.5 V; min 26.6 Ah (7 hr EVA), 9A peak, 5 yr,

<15.5 lbs (7 kg), 30 cycles

SAFER:42 V; 4.2 Ah (in emergency only)

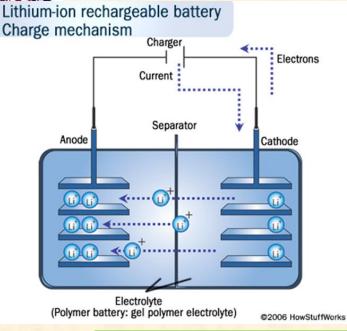
REBA: 12.5 V, 15 Ah, (7 hr EVA); 5 yr, ~6 lbs (2.7 kg)

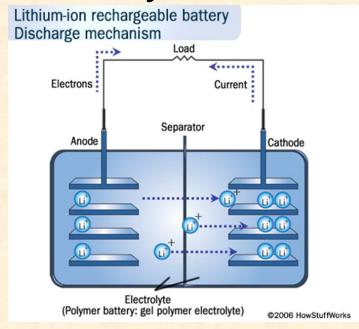
EHIP:6 V, 10.8 Ah; (7 hr EVA); 5 yr, ~1.8 lbs (0.8 kg)

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Lithium-ion Chemistry





The half reactions are:

Cathode: $LiMO_2 \rightarrow Li_{1-x}MO_2 + xLi^+ + xe^-$

Anode: $C + xLi^+ + xe^- \rightarrow Li_xC$

The overall reaction is: $LiMO_2 + C \Leftrightarrow Li_xC + Li_{1-x}MO_2$

Cathode: Lithium metal oxide (LiCoO₂, LiNi_{0.3}Co_{0.7}O₂, LiNiO₂, LiV₂O₅, LiMn₂O₄, LiNiO_{0.2}Co_{0.8}O₂)

Anode: Carbon compound (graphite, hard carbon, etc. or Li titanate or Sn alloy, Si alloy or Si/C)

Electrolyte: LiPF₆ and a combination of carbonates

Separator: PE or PP/PE/PP

Key Performance Parameters for Battery Technology Development Performance State-of-the-Art Current Value Threshold Goal

	Parameter			Value	
Safe, reliable operation	No fire or flame	Instrumentation/control- lers used to prevent unsafe conditions. There is no non- flammable electrolyte in SOA	Preliminary results indicate a moderate reduction in the performance with flame retardants and non-flammable electrolytes	Benign cell venting without fire or flame and reduce the likelihood and severity of a fire in the event of a thermal runaway	Tolerant to electrical and thermal abuse such as over-temperature, over-charge, reversal, and external short circuit with no fire or flame
Specific energy Lander: 150 – 210 Wh/kg 10 cycles	Battery-level specific energy*	90 Wh/kg at C/10 & 30°C 83 Wh/kg at C/10 & 0°C (MER rovers)	130 Wh/kg at C/10 & 30°C 120 Wh/kg at C/10 & 0°C	135 Wh/kg at C/10 & 0°C "High-Energy"** 150 Wh/kg at C/10 & 0°C "Ultra-High Energy"**	150 Wh/kg at C/10 & 0°C "High-Energy" 220 Wh/kg at C/10 & 0°C "Ultra-High Energy"
Rover: 150 – 200 Wh/kg EVA: 200 – 300 Wh/kg 100 cycles	Cell-level specific energy	130 Wh/kg at C/10 & 30°C 118 Wh/kg at C/10 & 0°C	150 Wh/kg at C/10 & 0°C	165 Wh/kg at C/10 & 0°C "High-Energy" 180 Wh/kg at C/10 & 0°C "Ultra-High Energy"	180 Wh/kg at C/10 & 0°C "High-Energy" 260 Wh/kg at C/10 & 0°C "Ultra-High Energy"
100 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0					

Li(Li_{0.17}Ni_{0.25}Mn_{0.58})O₂:

320 mAh/g MCMB

-50°C to +40°C

Battery values are assumed at 100% DOD, discharged at C/10 to 3.0 volts/cell, and at 0°C operating conditions

"Ultra-High Energy" = Exploration Technology Development Program cathode with Silicon composite anode

= Exploration Technology Development Program cathode with MCMB graphite anode

n/a

n/a

Assumes prismatic cell packaging for threshold values. Goal values include lightweight battery packaging.

240 mAh/g at C/10 & 25°C

 $Li(Li_{0.2}Ni_{0.13}Mn_{0.54}Co_{0.13})O_2$:

250 mAh/g at C/10 & 25°C 200 mAh/g at C/10 & 0°C

450 mAh/g Si composite

260 mAh/g at C/10 & 0°C

600 mAh/g at C/10 & 0°C

270 Wh/I "High-Energy"

385 Wh/I "High-Energy"

360 Wh/I "Ultra-High"

460 Wh/I "Ultra-High"

0°C to 30°C

with Si composite

280 mAh/g at C/10 & 0°C

1000 mAh/g at C/10 0°C

320 Wh/I "High-Energy"

390 Wh/I "High-Energy"

Revised 06/02/2008

420 Wh/I "Ultra-High"

530 Wh/I "Ultra-High"

0°C to 30°C

with Si composite

140 - 150 mAh/g typical

320 mAh/g (MCMB)

250 Wh/I

320 Wh/I

-20°C to +40°C

Energy density

EVA: 240 - 400 Wh/l

Lander: 311 Wh/l Rover: TBD

Operating

environment 0°C to 30°C, Vacuum Cathode-level

Li(Li,NiMn)O₂

Anode-level

Battery-level

energy density

density

Operating temperature

"High-Energy"

Cell-level energy

specific capacity

specific capacity

Customer Need

EVA: 200 – 300 Wh/kg 100 cycles

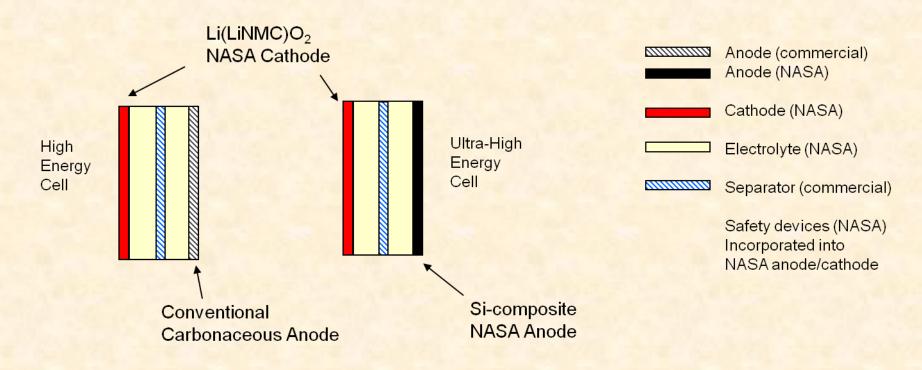


Space Power Systems (SPS) Li-ion Cell Development

- Component-level goals are being addressed through a combination of NASA in-house materials development efforts, NASA Research Announcement contracts (NRA), and grants
- Materials developed will be delivered to NASA and screened for their electrochemical and thermal performance, and compatibility with other candidate cell components
- Other activities funded through NASA can be leveraged NASA Small Business Innovative Research (SBIR) Program and Innovative Partnership Program (IPP)
- Leveraging off other government programs (DOD, DOE) for component-level technology
- Leveraging off other venues through Space Act Agreements (SAA) that involve partnerships with industry partners such as Exxon; nonprofit organizations such as Underwriters Laboratory (UL), etc.



Energy Storage Project Cell Development for Batteries



"High Energy" Cell

Baseline for EVA and Rover Lithiated-mixed-metal-oxide cathode / Graphite anode Li(LiNMC)O₂ / Conventional carbonaceous anode **150** Wh/kg (100% DOD) @ battery-level 0°C C/10 80% capacity retention at ~**2000** cycles

"Ultra-High Energy" Cell

Upgrade for EVA and Altair, possibly Rover
Lithiated-mixed-metal-oxide cathode / Silicon composite anode
Li(LiNMC)O₂ / silicon composite

220 Wh/kg (100% DOD) @ battery-level 0°C C/10
80% capacity retention at ~200 cycles



Cell Development

Assess components

- Build and test electrodes and screening cells (Coin and Pouch)
- Provide manufacturing perspective from the start

Scale-up components

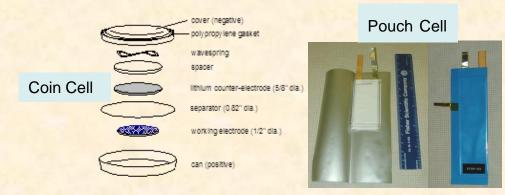
 Transition components from the lab to the manufacturing floor

Build baseline cells (10 Ah):

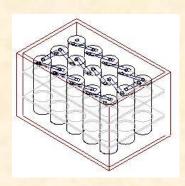
- graphite anode (MPG-111) with nickel-cobalt cathode (NCA)
- Determine baseline performance

Build and test evaluation cells (10 Ah):

- Determine component interactions
- Determine cell-level performance







NASA Goals:

Cathode Development Led by JPL

- Specific capacity of 280 mAh/g at C/10 and 0°C to 3.0 V
- High voltage operation to 4.8 V
- Improved thermal stability over conventional Li-ion cathodes

Te	echnology Challenges	Current Project Approaches to Address
_	gh specific capacity at actical discharge rates	 Vary stoichiometry to determine optimum chemical formulation Reduce particle size Experiment with different synthesis methods to produce materials with physical properties such that their specific capacity is retained on production scale
Lov	w volume per unit mass	 Vary cathode synthesis method to optimize properties that can: Improve energy density Improve ability to cast cathode powders Facilitate incorporation of oxide coatings, which have the potential to increase rate capability and reduce capacity fade to extend cycle life
irre	nimize 1st cycle eversible capacity loss d irreversible oxygen loss	•Surface modification via coatings to improve cathode-electrolyte interfacial properties •Improves capacity retention •Reduces capacity fade



Cathode Materials

System	Sp. Capacity, mAh/g		Voltage	Sp. Energy, Wh/kg (Cathode	TRL	Manufacturer (and
System	Theoretical	Experimental		Alone) vs Li		Heritage)
LiCoO ₂ (Lithiated Cobalt Oxide)	274	137	4.15	569	7-9	ABSL (Kepler, Aquarius, SMAP,EVA)
Li(NCO) (LiNi _{0.8} Co _{0.2} O ₂)	274	165	4.05	668	7-9	Yardney (Mars Missions, MER, MSL, GRAIL, Juno)
Li(NCA) (LiNi _{0.8} Co _{0.16} Al _{0.05} O ₂)	279	165	4.05	668	7-9	SAFT, Quallion, Yardney (Space Station, PGT)
LI (NMC) (0.83:0.83:0.83)	278	180	4.3	774	4	No
Li (Li,NMC)O ₂ Layered –layered Composites of LiMn ₂ O ₃ :LiMO ₂	330	275	4.5	1238	2-3	No
LiFePO ₄ (Olivine)	170	160	3.6	576	5	A123 (None)
LiCoPO ₄ (Olivine)	166	155	4.8	744	1-2	No
LiMnPO _{4 (} Olivine)	171	160	4.3	688	1-2	No
LiMn₂O₄ (Cubic Spinel)	148	120	4	480	4	No
LiMn _{1.5} Ni _{0.5} O ₄ (5 V Spinel)	148	130	4.8	624	4	No

Courtesy: Kumar Bugga, JPL

High Specific Energy Cathodes for Li-ion cells

Why Composite Electrode?

 Bi-functional electrode: Provide high capacity through 2D layer structure and high rate capability by 3D spinel structure

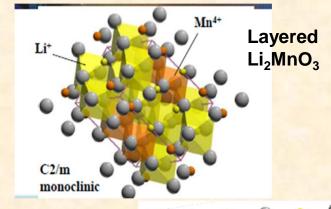
 Prevent oxygen loss during charge Enhance cathode stability through the spinel-layered or layered-layered integrated

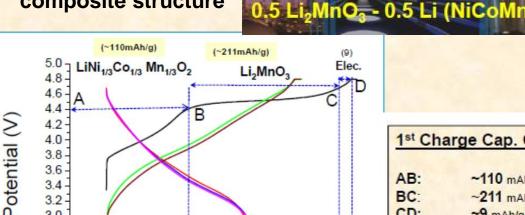
composite structure

3.2

3.0

2.8 2.6 2.4

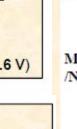




1st Charge Cap. Contributions:

AB: ~110 mAh/g (up to 4.4V) BC: ~211 mAh/g (4.4 - 4.6V)

CD: ~9 mAh/g Electrolyte (> 4.6 V)

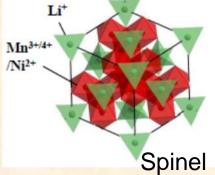


1st Discharge (calculated):

From LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂: 110 211 *1/2: 105.5

Total: 105.5 + 110 = 215.5 mAh/g

LiPF_e/EC-DMC-DEC (1:1:1) Li₂MnO₃: 300 100 150 200 250 350 Capacity (mAh/q)



(Lavered):

Li[Mn_{0.33}Ni_{0.33}Co_{0.33}]O₂

1st cycle: $Li_2Mn^{IV}O_3 \rightarrow Li_2O + MnO_2$ (C) $Li^+ + MnO_2 \rightarrow Li_{1.2}Mn^{\parallel l}O_3$ (D)

12JPL≡ NEI "D"

Courtesy: NEI Corporation

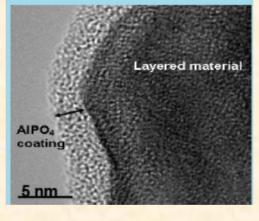
Cathode Efforts

Lithium Manganese rich Layered Layered Composites

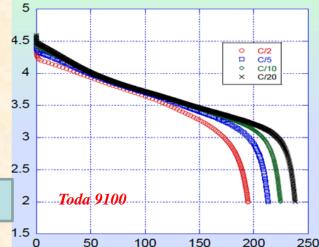
Strategies:

- Determine best ratio of Li, Ni, Mn and Co to maximize the capacity
- Add surface coating on cathode particles to improve the interfacial properties (reduces electrolyte reactivity and facilitates charge transfer)
- Improve morphology to create ultrafine spherical particles (vary synthesis method)

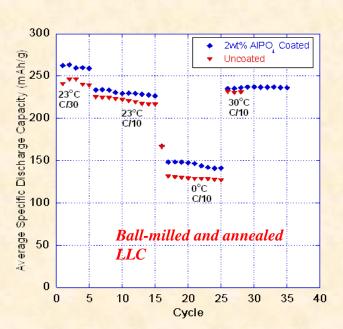
- High capacity > 250 mAh/g achieved from optimized composition of transition metal ratio and Li content
- High tap densities (1.5-2.0 g/cc) and spherical morphology realized from hydroxide precursor synthesis.
- Demonstrated improved performance (high reversible and low irreversible capacity, and cyclic and thermal stability with surface coatings, (AIPO₄ & LiCoPO₄)
- Developed new efficient coatings amenable for scale-up
- Evaluated cathode material of similar composition from several commercial sources.



Courtesy: Kumar Bugga, JPL



Toda 5th Discharge Rate Study



Anode Development Led by NASA GRC

- Goal: 1000 mAh/g at C/10 (10 hour discharge rate) and 0°C
 - Over 3 times the capacity of SOTA (State-of-the-art) Li-ion anodes
 - Threshold value = 600 mAh/g at C/10 and 0°C

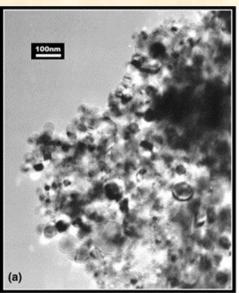
Technology Challenges	Current Approaches to Address
Minimize volume expansion during cycling	 Pursuing various approaches to optimize the anode structure to accommodate volume expansion of the silicon Nanostructured Si composite absorbs strain, resists active particle isolation on cycling Incorporation of elastic binders in Si –graphite and Si-C matrices Improvement of mechanical integrity by fabricating structure to allow for elastic deformation
Minimize irreversible capacity loss	 Protection of active sites with functional binder additives Pre-lithiation approaches are possible Nanostructured Si resists fracture and surface renewal
250 cycles	Loss of contact with active particles reduces cycle life. Addressing volume changes and improvement of mechanical integrity will improve cycle life

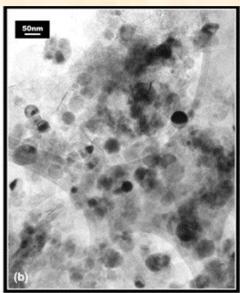


Si-C composites

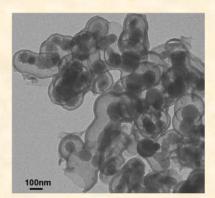
TEM of nanocrystalline Si

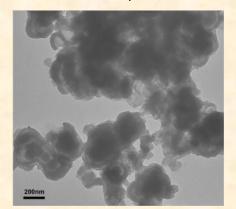
TEM of naocrystalline Si-C composites

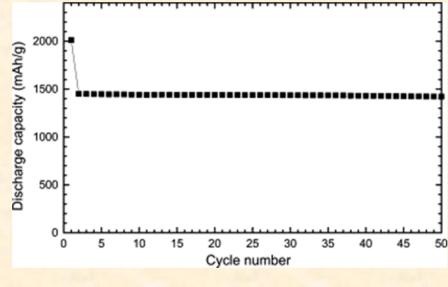


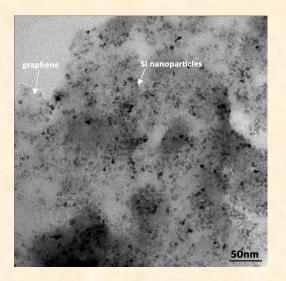


Wang, et.al Electrochem Communications, Vol 6, Issue 7, 2004,p .689









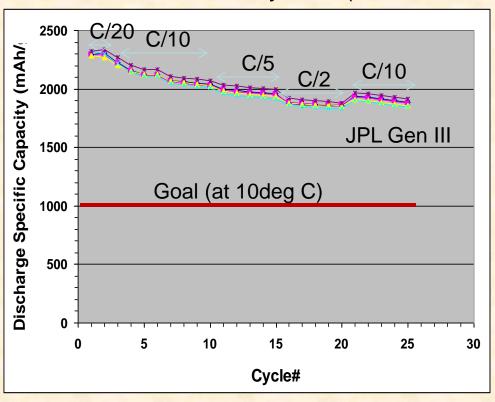
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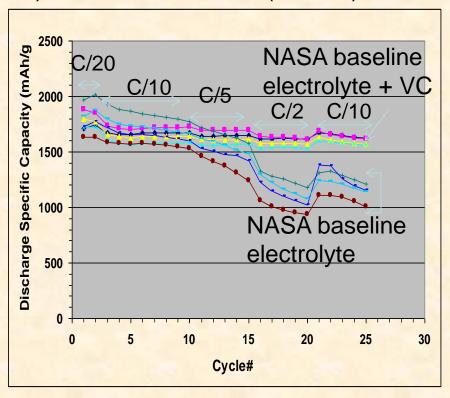


Si Anode Material Scale-up and Test

Si Anode made by Saft (2nd, calendared)

Si Anode (GT-4B)





- Saft successfully scaled up Si anode:
 Si anode made by Saft shows the highest capacity and excellent rate capability cycling which is much higher than 1000 mAh/g (the goal)
- VC in baseline electrolyte improves rate capability cycling



Current State for Safety of Li-ion Batteries

Although the chemistry is one that can provide very high energy density at this time, it is not the safest

 NASA human-rated safety requirement is two-fault tolerance to catastrophic failures – leakage of electrolyte (toxicity hazard), fire, thermal runaway

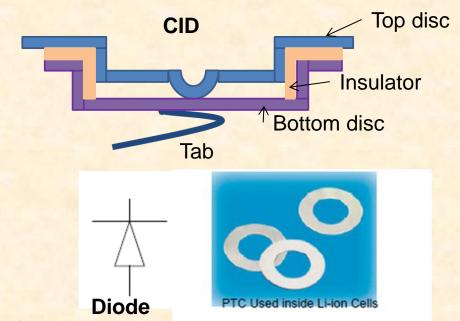
Hazards are encountered in Li-ion cells/ batteries typically during

- Overcharge/overvoltage
- External shorts
- Repeated overdischarge with subsequent charge
- High thermal environments
- Internal Shorts

Background

Lithium-ion cells, whether cylindrical, prismatic, etc. have different forms of internal protective devices

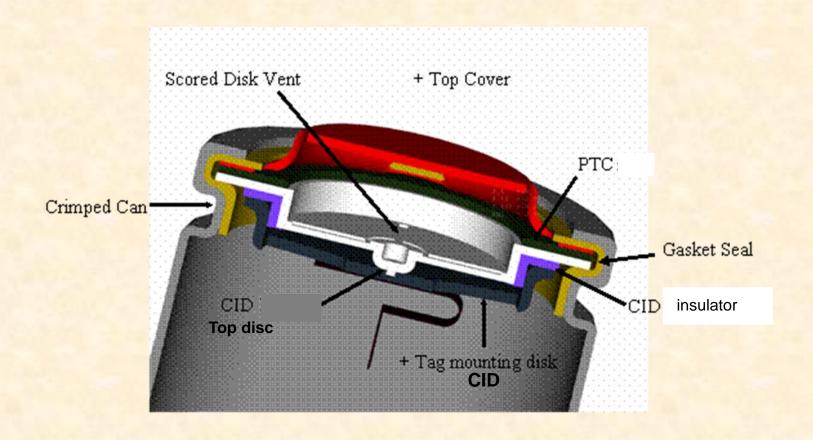
- PTC
- CID
- Tab/lead meltdown (fusible link type)
- Bimetallic disconnects
- etc.
- External protective devices used in lithium-ion battery designs are
 - Diodes
 - PTC/polyswitch
 - Thermal fuses (hard blow or resettable)
 - Circuit boards with specialized wire traces
 - etc.



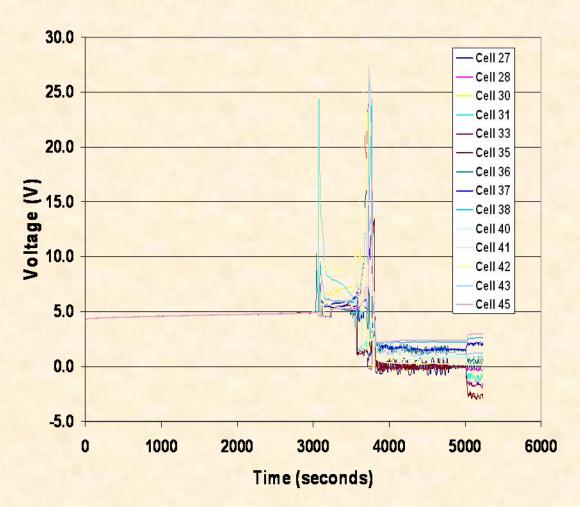
 Manufacturing quality is critical in preventing internal short hazards – cell quality as well as uniformity of cell performance is important



Schematic of Cell Header Portion



Overcharge Test on a 14-Cell String Showing Cell Voltages for the Sony Li-ion Cells

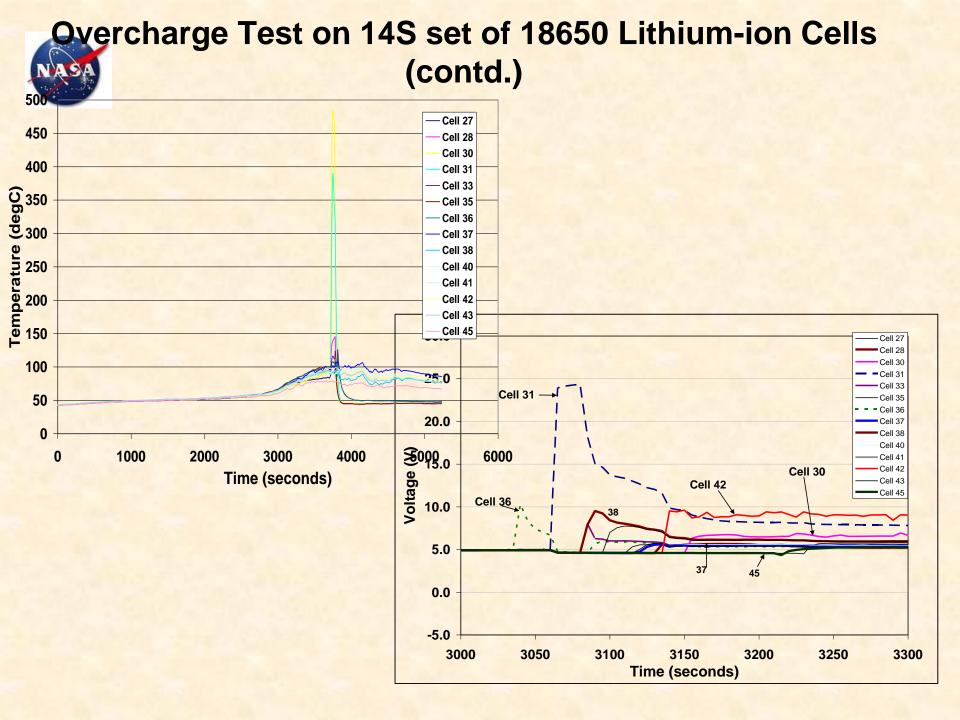






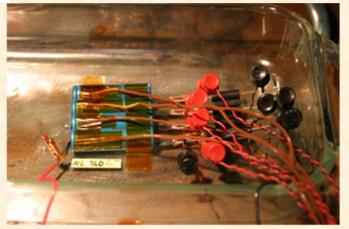
Missing: 27, 28, 30 and 31

Cells 37, 38 and 45 showed no visible Signs of venting





48V 6A Overcharge on 4P Battery



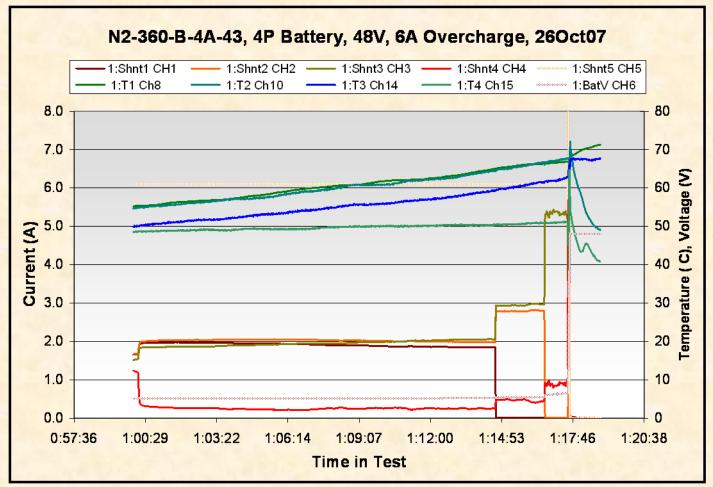






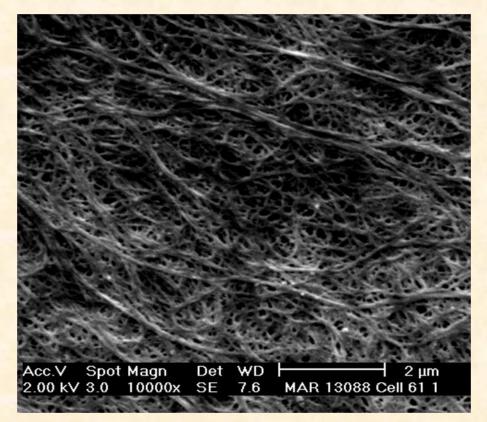


48V 6A Overcharge on 4P Battery

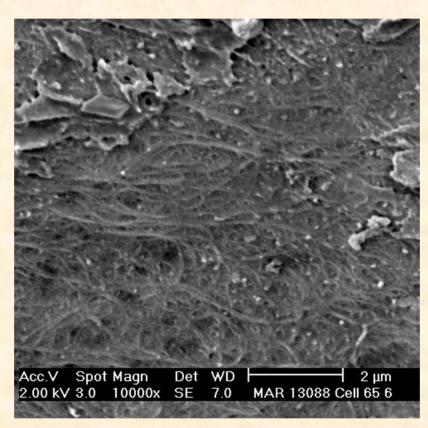


•The current on cell 4 in the parallel battery dropped low at ~1 hour into the overcharge; 14 minutes later the three other cells began to trip CID devices (a pop was audible) in sequence
•When the 3 cells dropped out, cell 4 was left carrying the 6A charge current.
•Cell 4 ruptured with flame (explosion); The cell can was split; temperature of the cell at the time of the event was 51°C

Current Separators in Commercial-off-the-Shelf Li-ion Cells



Unactivated Separator



Activated Separator

Shut-down temperature is very close to temperature at which initiation of thermal runaway occurs.

Electrolytes

Electrolyte Selection Criteria

- High conductivity over a wide range of temperatures
 - o 1 mS cm⁻¹ from -60 to 40°C
- Wide liquid range (low melting point)
 - o -60 to 75°C
- Good electrochemical stability
 - Stability over wide voltage window (0 to 4.5V)
 - Minimal oxidative degradation of solvents/salts
- Good chemical stability
- Good compatibility with chosen electrode couple
 - Good SEI characteristics on electrode
 - Facile lithium intercalation/de-intercalation kinetics
- Good thermal stability
- Good low temperature performance throughout life of cell
 - Good resilience to high temperature exposure
 - Minimal impedance build-up with cycling and/or storage
 - In addition, the electrolyte solutions should ideally have low flammability and be non-toxic !!



- Modification of electrolyte is one of the least invasive and cost effective ways to improve the safety characteristics of Li-ion cells. Common approaches include:
 - Use of Redox shuttles (to improve safety on overcharge)
 - lonic liquids (have inherently low flammability, due to low vapor pressure)
 - > Lithium salt modification
 - > Flame retardant additives
 - Use of non-flammable solvents (i.e., halogenated solvents)
- Of these approaches, the use of flame retardant additives has been observed to possess the least impact upon cell performance.

Development of Electrolytes Containing Flame

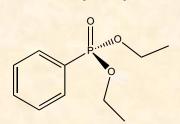
Retardant Additives

$$H_3CH_2C$$
 O
 CH_2CH_3
 CH_2CH_3

$$\begin{array}{c|c} \mathsf{H_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3} \\ & \mathsf{CH_2CH_2CH_2CH_3} \end{array}$$

Triethyl phosphate (TEP)

Tributyl phosphate (TBP)

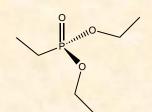


Triphenyl phosphite (TPPi)

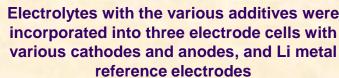
Bis-(2,2,2trifluoroethyl)methyl phosphonate (BTFEMP)

Diethyl phenylphosphonate (DPP)

Tris(2,2,2-trifluoroethyl) phosphite (TFPi)



Tris(2,2,2-trifluoroethyl) phosphate (TFPa)



Triphenyl phosphate (TPP)

TPP identified as

being the most robust

additive

flame retardant

1) Y. E. Hyung, D. R. Vissers, K. Amine J. Power Sources, 2003, 119-121, 383

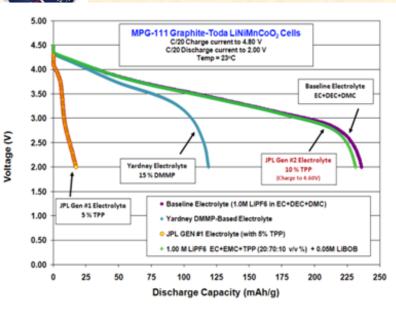
2) K. Xu, M. S. Ding, S. Zhang, J. L. Allen, T. R. Jow

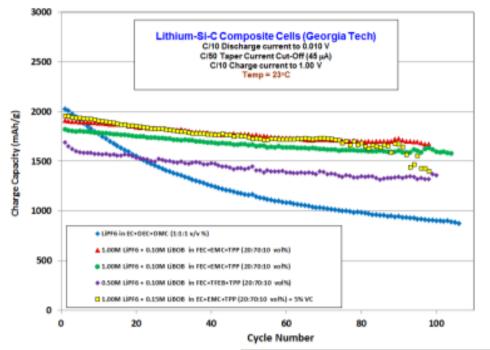
J. Electrochem. Soc. 2002, 149, A622

Smart, et.al., 219th Meeting of the Electrochemical Society, 2011

Electrolytes

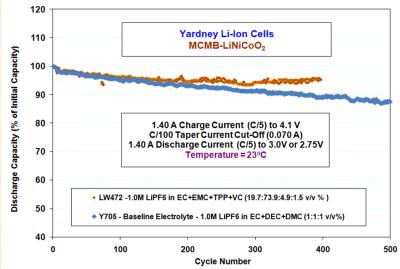






DMMP: Dimethyl Methyl phosphanate VC: Vinylene carbonate

LiBOB: Lithium bisoxalatoborate

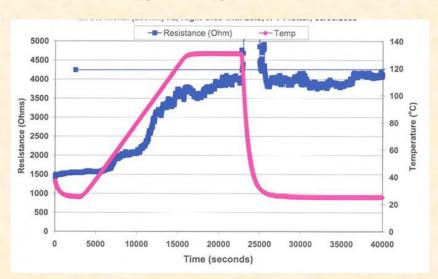


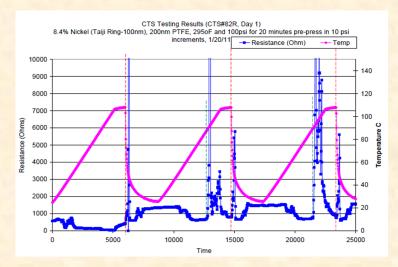
J. Jeevarajan, Ph.D. / NASA-JSC



Safety Component Development Led by NASA JSC

- Development of internal cell materials (active or inactive) designed to improve the inherent safety of the cell
 - Approach 1: Develop a high-voltage stable (phosphate type) coating on cathode particles to increase the safe operating voltage of the cell and reduce the thermal dissipation by the use of a high-voltage stable coating material. (Nano-sized material)
 - Approach 2: Develop a composite thermal switch to shutdown cell reactions safely using coatings on the current collector substrates (nano-particle metals)





PSI

PSI formed lithium metal phosphate coatings on metal oxide cathodes by thermal treatment of a mixture of metal phosphate and the cathode.

1 H. Lee, M. Kim, J. Cho, *Electrochemistry Communications*, 9 (2007) 149–154.

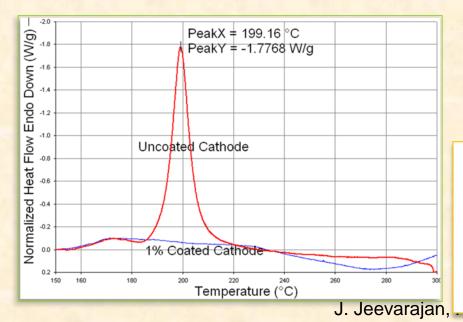
Benefits of Coating:

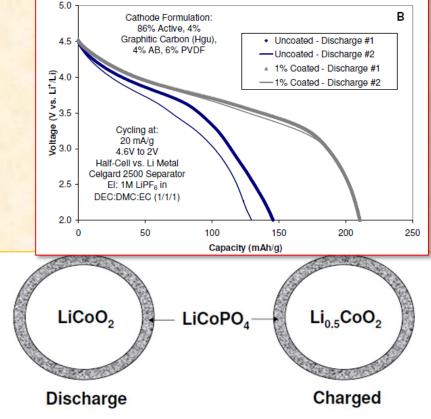
- Coating is a lithium conductor.
- Metal phosphates offer greater stability than their metal oxide counterparts.

Coating technique can be applied to protect any high energy density

cathode material.

 Common processing steps allow for low cost manufacturing.





NASA

Summary of Current Technology Work

High Energy NMC Cathodes

- Scale up of the NASA-process
- High Irreversible capacity loss, especially with uncoated cathode
 - Non-availability of lithium at the anode for the irreversible capacity.
- Electrolyte consumption (and anode dry out) due to O₂ evolved in formation
- Transition metal dissolution in electrolytes (Mn, Ni and Co)
- Low power densities, more noticeable with high electrode loadings
- Voltage slump during cycling due to "spinel formation"

Si composite anodes

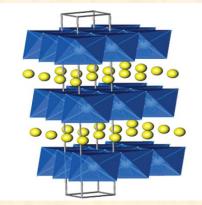
- Limited cycle life (< 500)
- High irreversible capacity (10-20%) and poor coulombic efficiency
- Unknown compatibility with the high energy cathode (dissolved metal?)

Electrolytes

Changes to the cathode or anode may require electrolyte modification

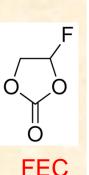
Cell Design

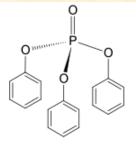
Test for performance and safety



HE-NMC Cathode



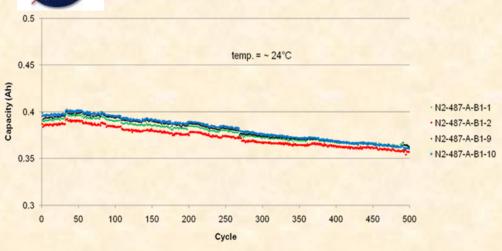


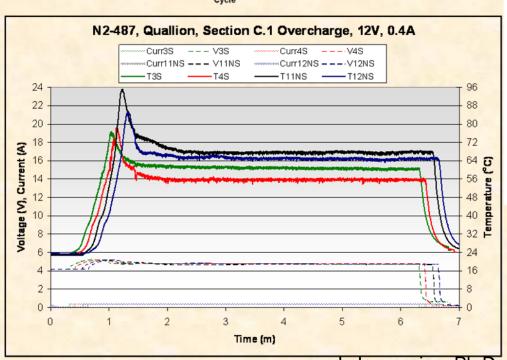


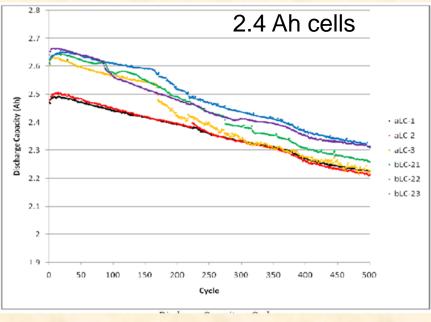
Triphenyl phosphate (TPP)



SafeLyte® Additive (IPP)







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Li-O₂ and Li-air: ~ TRL 2

Characteristics:
Ultra-low mass
600 to 2200 mAh/g of cathode
depending upon current density (rate)

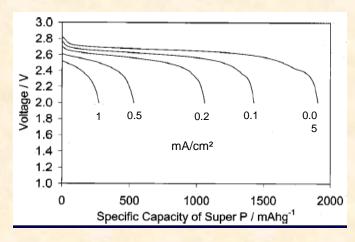
2.5 V avg. with 630 mAh/g carbon, 0.5 mA/cm²

Li-O ₂ and Li-air	Wh/kg	Wh/liter
electrochemical	587	880
pouch cell	473	617

2.3 V avg. with 300 mAh/g carbon, 1.0 mA/cm²

Li-O ₂ and Li-air	Wh/kg	Wh/liter
electrochemical	329	526
pouch cell	279	381

^{*}Projections are for "free" air (neglect O2 storage)



Journal of The Electrochemical Society, 149 (9) A1190-A1195 (2002)

Challenges:

- Recharge capability
- Capacity of carbon to store Li discharge products

Rate capability

Oxygen storage type	Wh/kg	Wh/liter
steel	375	419
carbon composite	438	427
no storage	473	617



Li-S: ~ TRL 3

Characteristics:

High specific capacity (1600 mAh/g S theoretical)
2-plateau discharge

Projection for 2-plateau discharge Assume 1000 mAh/g S

Li-S	Wh/kg	Wh/liter
electrochemical	610	864
pouch cell	474	595

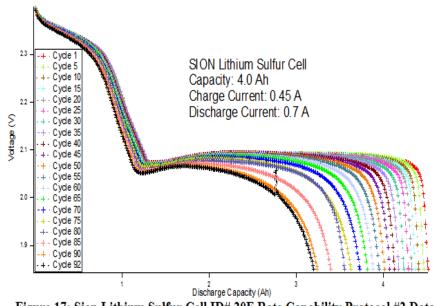


Figure 17: Sion Lithium Sulfur Cell ID# 20F Rate Capability Protocol #2 Data

Demonstrated in 4 Ah pouch cells (JSC):

BOL: 393 Wh/kg EOL: 256 Wh/kg

75 cycles to 80% of initial capacity

Challenges:

Safety (rechargeability, lithium

dendrite formation)

Cycle life







Summary

- Power is needed for all Exploration vehicles and for the mission applications.
- For long term missions as in NEA (near earth asteroid) and Mars programs, safe, high energy/ultra high energy batteries are required.
- Component level research will provide higher energy density as well as safer lithium-ion cells for human-rated space applications. The challenge is with scale-up of materials and cell size and proof of safety in larger cell designs.
- Collaborations with other government agencies and industry provide good leverage.
- NRA, grants, SBIR and STTR allow us to take significantly good research into production even though space applications require only low volume production.



Acknowledgment

- Coworkers in Power Systems Branch at JSC and other NASA Centers
- Collaborators in industry and academia